



## Mixing Rules of Dielectric Properties of Aqueous Organic Solution

GUO ZHU JIA<sup>1,2,\*</sup>, XIAO QING YANG<sup>2</sup> and KA MA HUANG<sup>2</sup>

<sup>1</sup>College of Physics and Electronics Engineering, Sichuan Normal University, Chengdu 610066, P.R. China

<sup>2</sup>College of Electronics and Information Engineering, Sichuan University, Chengdu 610064, P.R. China

\*Corresponding author: Fax: +86 28 84767058; Tel: +86 28 84480798; E-mail: jia1689500@126.com

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Many dielectric properties of aqueous organic solution over the microwave frequency have been investigated, their frequency-dependent dielectric properties can be summarized by three parameters in the Debye equation *i.e.*, a static dielectric constant, a high-frequency limiting dielectric constant and a dielectric relaxation time constant. On the basis of electrostatics, rate theory, solution thermodynamics and hydrogen bond dynamics we have summarized dielectric "mixing rules" that describe the frequency-dependent dielectric properties of the solvent organic aqueous solution based on solution composition and the dielectric parameters for the solution components. These "mixing rules" yield good agreement between the predicted and experimental dielectric properties of DMF-water mixtures over all solution compositions.

**Key Words:** Hydrogen-bond, Mixing rules, Organic aqueous solution, Dielectric, Microwave.

### INTRODUCTION

Microwave heating has attracted interest in the chemical industry for its ability to provide targeted heating of liquids rapidly and uniformly<sup>1-3</sup>. For better application of microwaves in the chemical industry, the interaction between microwaves and the mixtures needs to be further studied. Usually, the permittivity describes a material's ability to absorb, transmit and reflect electromagnetic energy. Thus, it is important to know the permittivity of liquid mixtures at microwave frequencies. The dielectric properties of binary mixtures have been the subject of experimental and theoretical investigation for many decades. Many researchers have studied the dielectric properties of binary mixtures using time domain reflectometry (TDR)<sup>4</sup> and a resonant cavity perturbation method (RCPM)<sup>5,6</sup> in order to understand their intermolecular interactions and dynamics.

Water is the solvent for a large body of chemical reactions that take place in chemical and biological systems. The distinctive properties of water are believed to depend fundamentally on the microscopic characteristics of hydrogen-bond (HB). At a fundamental level, the frequency-dependent dielectric behaviour of solvent mixtures provides information on molecular interactions and mechanisms of molecular processes<sup>7-11</sup>.

Most available dielectric data at microwave frequencies are for heterogeneous items such as foods, geological materials and biological samples and these values can vary remarkably due to compositional variations based on their source.

Continuous frequency-dependent dielectric spectra have been collected for certain solvents. However, these studies focused on the dielectric properties of binary mixtures of two different alcohols and alcohols with water have been studied in detail with an emphasis on the formation of hydrogen-bonded complexes and the presence of cooperative relaxation processes for different molecular clusters. The characterization of the dielectric properties of solvent mixtures at microwave frequencies has both fundamental and practical utility.

We have determined that the frequency-dependent dielectric behaviours of both pure solvents and water mixtures over this frequency range can be described well by three parameters *viz.*, a static dielectric constant, a high-frequency limiting dielectric constant and a dielectric relaxation time constant that characterizes the dipolar rotational process of the molecular species. We have used these parameters to develop "mixing rules" based on solution thermodynamics, electrostatics and hydrogen bond dynamics that describe the frequency-dependent dielectric behaviour of solvent mixtures. This paper describes the development of these "mixing rules" and demonstrates the effectiveness of this approach for estimating the dielectric properties of solvent mixtures at microwave frequencies. The experimental dielectric spectra were fitted in a complex nonlinear least-squares routine by using various models represented by the Havriliak-Nsolvantami function<sup>7</sup>.

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{[1 + (j\omega\tau)^{1-\alpha}]^{\beta}} = \epsilon' + j\epsilon'' \quad (1)$$

where  $\epsilon_0$  is the static permittivity,  $\epsilon_\infty$  is the high-frequency limiting permittivity and  $\tau$  is the relaxation time.  $\alpha$  and  $\beta$  are shape parameters describing symmetric and asymmetric distribution of relaxation times, respectively.

## EXPERIMENTAL

### Dielectric "Mixing rules"

The Debye equation requires three parameters ( $\epsilon_0$ ,  $\tau$ ,  $\epsilon_\infty$ ) to describe the frequency-dependent dielectric relaxation behaviour of binary mixtures. In this paper, we investigated the three parameters of the solvent mixtures that are related to those of the pure solvents through appropriate dielectric "mixing rules".

**Dielectric relaxation time:** Dielectric relaxation refers to the relaxation response of a dielectric medium to an external electric field of microwave frequencies. This relaxation is often described in terms of the permittivity as a function of frequency that can be described by the Debye equation. A mixing formula for the relaxation time  $\tau$  at a constant temperature was proposed by Lou *et al.*<sup>10</sup>.

$$\ln \tau_{\text{mix}} = x_1 \ln \tau_1 + x_2 \ln \tau_2 \quad (2)$$

where the subscripts 1 and 2 represent the two solvents, respectively and  $x_1$ ,  $x_2$  and ( $x_1 + x_2 = 1$ ) are the volume fractions of the respective components. This type of variation suggests that intermolecular association is taking place in this binary system and solute-water interactions induced hydrogen bond produce a field such that the effective dipoles rotate more slowly.

**High-Frequency dielectric constant:** The value for solvent mixtures can be calculated based on theoretical models as well as many empirical formulas. In this paper, a simple model has proven to be sufficient to calculate the value for solvent mixtures<sup>10</sup>.

$$\frac{1}{\epsilon_{\infty, \text{mix}}} = \frac{x_1}{\epsilon_{\infty, 1}} + \frac{x_2}{\epsilon_{\infty, 2}} \quad (3)$$

**Static dielectric constant:** Several dielectric mixture equations have been used in the literature to estimate the dielectric properties of binary mixtures. Many equations have proven to be applicable to the experimental data in the preceding literature. One of the most successful methods of modeling the dielectric constant of liquids is due to Onsager and later a considerably improved model was due to Kirkwood<sup>8</sup>. Another dielectric constant equation for a dilute dispersion of spherical inclusions was developed by Bruggeman, based on electrostatics<sup>10</sup>:

$$\left( \frac{\epsilon_{\text{mix}} - \epsilon_1}{\epsilon_2 - \epsilon_1} \right) \left( \frac{\epsilon_2}{\epsilon_{\text{mix}}} \right)^{\frac{1}{3}} = 1 - x \quad (4)$$

where the subscripts 1 and 2 denote the two solvent components, respectively and  $x$  is the volume fraction of the dispersed phase.

An array of experiments and theories have revealed the dielectric path ways and timescales associated with different aspects of the hydrogen-bond (HB) dynamics of bulk water and aqueous solution<sup>8-11</sup>. Thus, this implies that a new formula

needs to be formulated to include hydrogen bond contributions. The static permittivity for the mixtures can be explained using the Luzar model by assuming the formation of two types of hydrogen-bonded dimers. The Kirkwood correlation factor  $g_i$  for a mixture can be expressed as:

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{9\epsilon_0} = \frac{4\pi}{9kT} \sum_{i=1}^2 g_i \rho_i \mu_i^2 \quad (5)$$

where  $i = 1$  and  $2$  represent solvent and water, respectively. Here,  $\mu_i$  is the dipole moment of an solvent or water molecule,  $\rho_i$  is the density and  $g_i$  is the Kirkwood correlation factor for the  $i$ th liquid component. The interpretation of the dielectric phenomena in terms of the Kirkwood correlation factor is very difficult for a mixture of associated compounds. It is impossible to separate the average correlation factors  $g_1$  and  $g_2$  from a single value of the static dielectric constant without any assumptions. Kirkwood-Frohlich theory must be applied to media containing two species of molecules and the cross-correlation terms must be taken into account to separate  $g_1$  and  $g_2$  when considering only the hydrogen-bond contribution to the dipole-dipole correlation. In the present approach, the Kirkwood correlation factors for individual species  $i = 1$  and  $2$  are modified and these new correlations are described by the following relations:

$$g_1 = 1 + Z_{11} \cos \phi_{11} + Z_{12} \cos \phi_{12} \left( \frac{\mu_1}{\mu_2} \right) \quad (6)$$

$$g_2 = 1 + Z_{21} \cos \phi_{21} \left( \frac{\mu_2}{\mu_1} \right) \quad (7)$$

where  $Z_{11} = 2 \langle \text{nHB11} \rangle$ ,  $Z_{12} = 2 \langle \text{nHB12} \rangle$  and  $Z_{21} = -\langle \text{nHB12} \rangle / 2$ , are the average numbers of hydrogen bonds between solvent-solvent, solvent-water and water-water pairs, respectively.  $\phi_{11}$ ,  $\phi_{12}$  and  $\phi_{21}$  are the average angles between neighboring dipoles of solvent-solvent, solvent-water and water-water pairs, respectively and  $\cos \phi_{ij}$  is taken to be  $1/3$ . The average number of hydrogen bonds [ $\langle \text{nHB11} \rangle$ ,  $\langle \text{nHB22} \rangle$  and  $\langle \text{nHB12} \rangle$ ] per solvent molecule for  $1i$  pairs ( $i = 1$  or  $2$ ) has been determined using following relation<sup>9</sup>:

$$\langle \text{n}_{\text{nb}}^{\text{li}} \rangle = \frac{n_{\text{li}} \omega^{\text{li}}}{n_1} \quad (8)$$

where  $\omega^{\text{li}} = 1/[1 + \alpha \exp(\beta E_{1i})]$  is the probability of bond formation between solvent and water.  $n_1$  is the number density of solvent molecules,  $\beta = 1/kT$  and  $\alpha^{\text{li}}$  are the statistical volume ratios of the two subvolumes of the phase space related to the nonhydrogen-bonded and hydrogen-bonded pairs. These hydrogen-bonded pairs have only two energy levels,  $E_{11}$  and  $E_{12}$ , for  $11$  and  $12$  pair-formed bonds, respectively. The values of,  $\langle \text{nHB12} \rangle$  and  $\langle \text{nHB11} \rangle$  depend on the number densities of the hydrogen-bonded pairs between Solvent or water ( $n_{12}$ ) and between solvent molecules ( $n_{11} = 2n_1 - n_{12}$ ), respectively. These can be calculated, during which solvent-solvent ( $11$  pair) and solvent-water ( $12$  pair) are formed.

The concentration dependence of the static dielectric constants is calculated using eqns. 7-10 and is compared with experimental data. Here, the parameters required in eqns. are the dipole moments of molecules solvent. The polarizability,

static volume ratio, number of hydrogen bonds and bonding energy are the fitting parameters. We calculated the average number of hydrogen-bonded solvent-solvent pairs,  $\langle n_{HB11} \rangle_v$  and solvent-solvent pairs,  $\langle n_{HB12} \rangle_v$ , per unit volume ( $\text{cm}^3$ ) using

$$\langle n_{HB11} \rangle_v = \frac{C_1 \rho_{\text{mix}} N_A n_{HB11}}{M_1} \quad (9)$$

$$\langle n_{HB12} \rangle_v = \frac{C_1 \rho_{\text{mix}} N_A n_{HB12}}{M_1} \quad (10)$$

Here, solvent is the weight fraction of solvent,  $\rho_{\text{mix}}$  ( $\text{g}/\text{cm}^3$ ) is the density of the mixtures,  $N_A$  is the Avogadro number and  $M_1$  is the molecular weight of solvent.

As shown in Fig. 1, the model gives a good qualitative account of the dielectric constant of the DMF-water mixtures. In present analysis, the best possible values of molecular parameters with which the theoretical static dielectric constant values are in reasonable agreement with the experimental values. For aqueous organic solution, one of the mixture constituent molecules acts as 'structure-breaker' and hence there is a decrease in the total number of aligned effective dipoles that contributed to the mixture dielectric polarization.

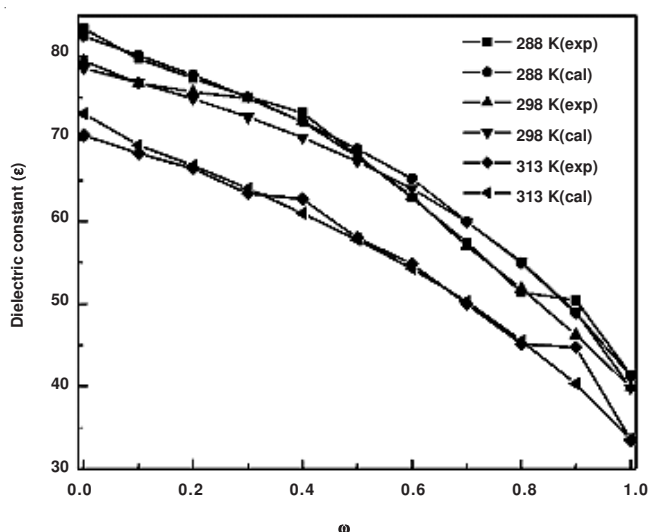


Fig. 1. Concentration dependency for static dielectric constant of DMF-H<sub>2</sub>O mixture exp denotes the value of experiment in literature<sup>3</sup> and cal denotes the value of calculation

## RESULTS AND DISCUSSION

The compositions dependence of the dielectric relaxation behaviour at microwave frequencies of aqueous organic solution was investigated over the whole composition range. These mixtures exhibit different relaxation dynamics in different concentration regions. For static dielectric constant, A hydrogen-bonding configuration in mixtures is suggested, where a water molecule in a hydrogen-bonding network is replaced by an organic polarity molecule. Through this configuration, the breakdown of water structure is introduced. On the basis of electrostatics, rate theory, solution thermodynamics and hydrogen dynamics we have summarized dielectric "mixing rules" that describe the frequency-dependent dielectric properties of the solvent organic aqueous solution based on solution composition and the dielectric parameters for the solution components. These "mixing rules" yield good agreement between the predicted and experimental dielectric properties for the DMF-water mixtures over all solution compositions.

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